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Nonlinear refractive index and three-photon absorption coefficient of poly(9,9-dioctylfluorence)

J. I. Jang,[1,a)] S. Mani,[1] J. B. Ketterson,[1,2] P. Lovera,[3] and G. Redmond[4]
[1]*Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road Evanston, Illinois 60208, USA*
[2]*Department of Electrical Engineering and Computer Science, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA*
[3]*Nanotechnology Group, Tyndall National Institute, Lee Maltings, Prospect Row, Cork, Ireland*
[4]*School of Physics and School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland*

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We investigate the optical Kerr effect and third harmonic generation (THG) arising from $\chi^{(3)}$ of poly(9,9-dioctylfluorence), which is an emerging organic π-conjugated polymer from the perspective of diverse optoelectronic applications. The measured nonlinear refractive index, obtained with closed-aperture Z-scan, is $n_2=(2.04\pm0.10)\times10^{-12}$ esu at $\lambda=1540$ nm. Open-aperture Z-scan yields the three-photon absorption coefficient of $\gamma=(1.88\pm0.26)\times10^{-3}$ cm^3/GW^2 at $\lambda=1064$ nm, arising from $\chi^{(5)}$ response. The wavelength-dependent THG indicates that this semiconducting polymer can be a potentially useful polymer system for nonlinear-optics applications involving high-order optical processes in the mid-IR range. © *2009 American Institute of Physics*. [doi:10.1063/1.3269588]

Nonlinear optical response from organic polymers and its connection to chemical structures are well understood both theoretically and experimentally.[1] Various phenomena observed from this class of materials such as the optical Kerr effect, third harmonic generation (THG), two-photon absorption, four-wave mixing, and Raman scattering arise due to the third-order nonlinear optical susceptibility, $\chi^{(3)}$, which is nonzero even in centrosymmetric materials.[2] Compared with bulk inorganic counterparts, organic polymers provide a unique opportunity to control or improve their nonlinear optical properties basically due to diverse molecular designs accompanied by various synthesis techniques. Since the first discovery of a large $\chi^{(3)}$ in polydiacetylene *p*-toluene sulfonate,[3] organic π-conjugated polymers have especially attracted attention from the nonlinear optics community. The third-order nonlinear response from organic π-conjugated polymers is known to be sensitive to the π-conjugation length and proportional to E_g^{-6}, where E_g is the bandgap energy.[4] Typical values of $\chi^{(3)}$ of organic π-conjugated polymers have a broad range and can reach to 10^{-5} esu for the resonant case.[5] However, most of them have relatively low optical transparencies and/or damage thresholds.[2]

Polyfluorenes and their π-conjugated derivatives are actively researched organic polymers with excellent optical and electronic as well as structural properties.[6,7] Their efficient photoluminescence, electroluminescence, and high charged-carrier mobility, coupled with thermotropic liquid crystallinity, have been utilized for various optoelectronic devices including light-emitting diodes, field-effect transistors, polymer-based lasers, and display applications.[8–13] Poly(9,9-dioctylfluorene) (PFO) is a standard liquid-crystalline homopolymer, composed of planar biphenyl units linked by a carbon atom in position 9 (see the inset of Fig. 1). Figure 1 displays a typical room-temperature absorption spectrum obtained from PFO using a white-light source. This strong and broad absorption arises from a featureless $\pi-\pi^*$ transition, which is characteristic of many organic π-conjugated polymers.[6] The optical bandgap of PFO, defined by the onset of strong absorption, is about 2.95 eV and the corresponding emission under external excitation is very efficient with rich spectral features depending on its phase.[14] Recently, PFO nanowires with excellent optical and electronic properties were synthesized by the method of solution-assisted template wetting, which could be utilized for nanoscale optoelectronic applications.[15]

Polyfluorenes are also optically active under strong two- and three-photon excitation.[16,17] However, their nonlinear optical parameters such as $\chi^{(3)}$ and $\chi^{(5)}$ have not been studied up to date. In this letter, we report the measurement of the nonlinear refractive index $n_2 \propto \mathrm{Re}\,\chi^{(3)}/n_0$ and the three-photon absorption coefficient $\gamma \propto \mathrm{Im}\,\chi^{(5)}/n_0^3$ of PFO, n_0 being the linear refractive index, far away from resonance using the single-beam Z-scan technique.[18] The third-order nonlinear optical response is also confirmed by THG that shows a strong wavelength dependence near the optical

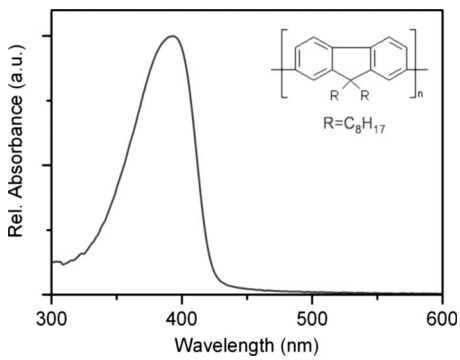

FIG. 1. Room-temperature absorption spectrum of PFO solution (6 mg/mL in chloroform). The inset shows the chemical structure of PFO.

a)Electronic mail: joon-jang@northwestern.edu.

bandgap of PFO. Together with its versatile properties for optoelectronic applications, PFO could also be used for nonlinear optical applications owing to its structural stability, optical transparency, and high damage threshold.

Z-scan is a widely used technique to characterize both n_2 and the multiphoton absorption coefficient of a nonlinear material by using the closed- and open-aperture Z-scan configurations, respectively.[18–20] We first measured γ with open-aperture Z-scan, employing a Q-switched, mode-locked Nd:YAG laser ($\lambda=1064$ nm). The corresponding laser pulse width is about 30 ps and the repetition rate is 10 Hz. Our experiments were performed on a solution prepared by dissolving PFO in chloroform (6 mg/mL). This clear PFO solution was contained in a glass vial of thickness $L=1$ mm. The incident laser beam was focused using a converging lens onto the sample, which was mounted on a computer-controlled translation stage to move along the z-axis near the focal plane of the lens. The transmittance, $T(z)$, through a finite aperture was measured as a function of z in the far field. A reference beam, obtained by splitting the input beam, was monitored to compensate for laser fluctuations. The output of the signal and reference photomultiplier tubes was fed to separate boxcar integrators, and read out using a data acquisition system. We have confirmed that the contribution from pure chloroform to the Z-scan results were negligible.

Figure 2(a) shows the normalized $T(z)$ of PFO obtained from open-aperture Z-scan, showing nonlinear three-photon absorption in PFO at $\lambda=1064$ nm. The solid curve is a best fit with $p_0=0.41$ at the focus using the equation for three-photon absorption,[19] which is given by

$$T(z)=\frac{1}{\pi^{1/2}p_0}\int_{-\infty}^{\infty}\ln\{[1+p_0^2\exp(-2x^2)]^{1/2}+p_0 \times\exp(-x^2)\}dx, \quad (1)$$

where $p_0(z)=[(2\gamma I_0^2 L_{eff})/(1+z^2/z_0^2)]^{1/2}$, $z_0=\pi\omega_0^2/\lambda$ is the Rayleigh range, ω_0 is the beam waist at the focus, and $L_{eff}=(1-e^{-2\alpha L})/2\alpha$ is the effective sample thickness. Based on our linear absorption measurement, we found that the linear absorption coefficient, α, is negligible at 1064 nm, thus $L_{eff}\simeq L=1$ mm. Using the on-axis beam irradiance $I_0=30$ GW/cm^2, the three-photon absorption coefficient is given by $\gamma=(1.88\pm0.26)\times10^{-3}$ cm^3/GW^2. We also directly confirmed that PFO is three-photon active by monitoring the power dependence of the photoluminescence (PL) at 1064 nm. Figure 2(b) shows the three-photon-induced PL spectra observed in the range of 437–465 nm for several excitation levels, $I_0=1.6$–16.1 GW/cm^2. The corresponding PL peak intensities (dots) are plotted in Fig. 2(c) and superimposed by an empirical cubic fit (solid trace). The PL detection setup was the same as that for the THG experiments described below.

In the closed-aperture Z-scan, however, we found that strong three-photon absorption at $\lambda=1064$ nm obscures the nonlinear refraction effects. In order to measure a *nonresonant* n_2, we used an optical parametric amplifier (OPA) tuned to $\lambda_{OPA}=1540$ nm, which was synchronously driven by the Nd:YAG laser. We carefully chose λ_{OPA} such that it is far below the threshold for three-photon excitation. Our closed-aperture Z-scan was calibrated by using carbon disulfide (CS_2) as a reference nonlinear material ($n_2[CS_2]=1.3\times10^{-11}$ esu).[21] As shown in Fig. 3, the normalized closed-aperture Z-scan trace of PFO exhibits a peak-valley configuration, indicating positive nonlinearity of the material. Transmittance change at the detector (ΔT) is related to the on-axis phase shift at the focus ($\Delta\phi$) by

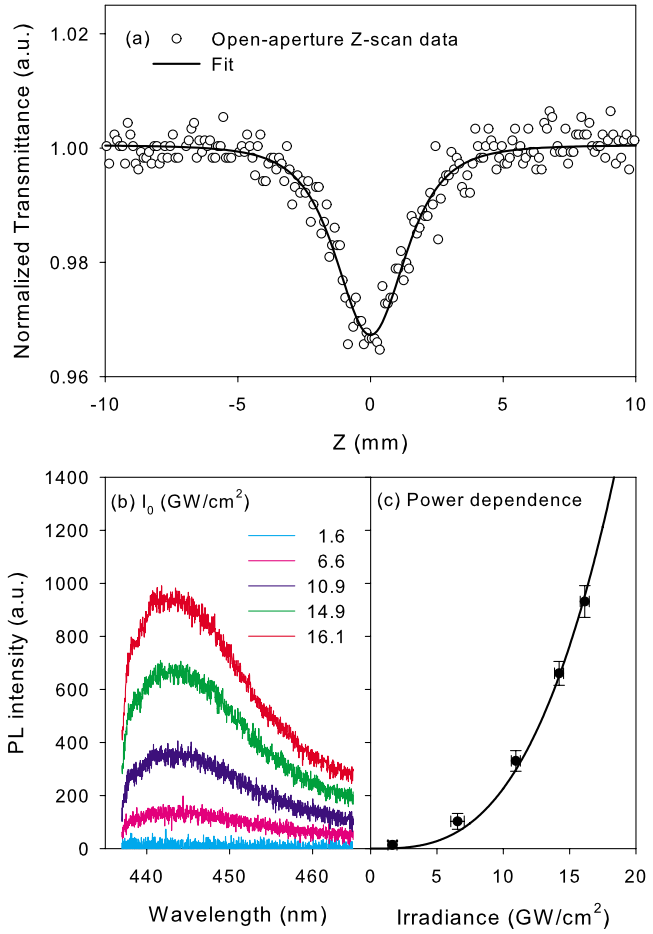

FIG. 2. (Color online) (a) Normalized open-aperture Z-scan data ($S=1$) showing three-photon absorption at $\lambda=1064$ nm and input irradiance $I_0=30$ GW/cm^2. The fit (solid curve) was obtained with three-photon absorption coefficient $\gamma=1.88\times10^{-3}$ cm^3/GW^2. (b) Three-photon-induced PL spectra from PFO under several excitation levels. (c) The corresponding peak intensities as a function of I_0 were plotted by the dots. The solid trace is a cubic fit to the data.

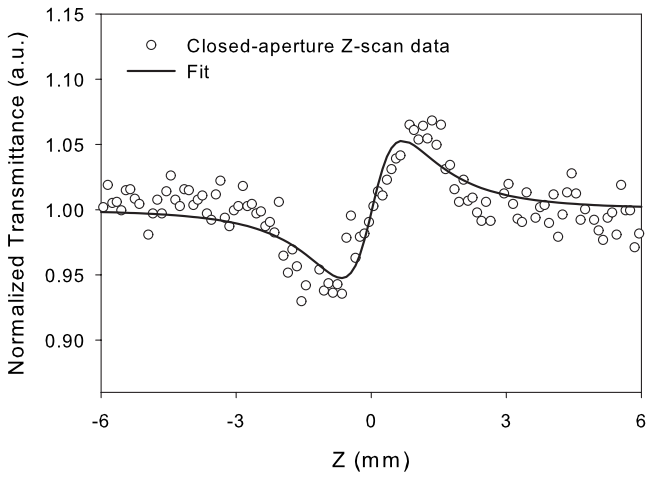

FIG. 3. Normalized closed-aperture Z-scan data ($S=0.6$) at $\lambda_{OPA}=1540$ nm and input irradiance $I=16$ GW/cm^2. The solid curve represents a theoretical fit obtained with $n_2=2.04\times10^{-12}$ esu.

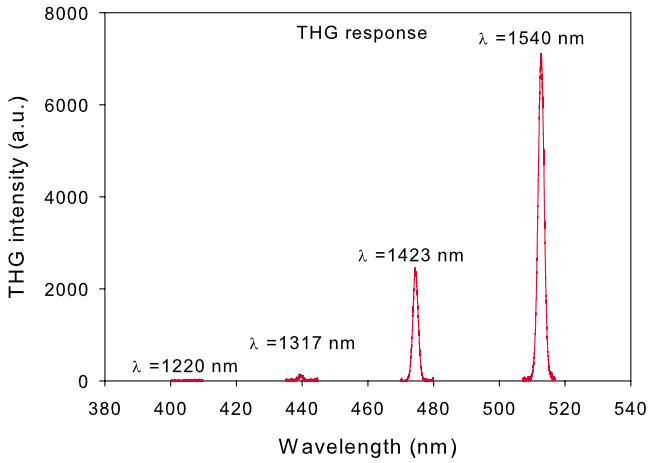

FIG. 4. (Color online) Wavelength-dependent THG from PFO. The significant decrease in the THG intensity near the bandgap arises from efficient three-photon generation of charged carriers.

$$\Delta T \simeq 0.406(1-S)^{0.25}\Delta\phi = 0.406(1-S)^{0.25}\frac{2\pi}{\lambda}L_{eff}\Delta n, \tag{2}$$

where S is the aperture linear transmittance and Δn is the on-axis index change at the focus, which is given by $\Delta n = n_2 I_0$. The solid curve is a least-square fit to the data obtained with $\Delta\phi = 0.34$ and 60% transmittance of the aperture ($S=0.6$) at $I_0 = 16$ GW/cm^2, yielding $n_2 = (2.04 \pm 0.10) \times 10^{-12}$ esu. Although the measured n_2 value of PFO is just moderate, primarily due to its large bandgap energy, we emphasize that this n_2 value was obtained from randomly oriented PFO dissolved in chloroform, implying that pristine PFO, especially in a nanowire form, may have a much larger n_2 value. Also, it is important to note that the material has high environmental stability and optical transparency as well as a damage threshold higher than 30 GW/cm^2.[17] Moreover, we can potentially improve the third-order nonlinearity further by introducing electron donor and acceptor groups into a conjugated system.[22]

The origin of the measured refractive nonlinearity in PFO is attributed to bound electronic effects and is confirmed by its THG response using laser pulses from the OPA. For THG experiments, PFO solution with the same concentration (6 mg/mL in chloroform) was loaded into a 12 mm thick vial to increase the THG interaction length. The incident beam with λ_{OPA} in the range of 1220 to 1540 nm was focused onto a spot 500 μm in diameter using a 3 cm focal-length lens. The incident photon energy was about 0.95 mJ/pulse and the corresponding irradiance was about 16 GW/cm^2. The THG signal was collected in a transmission geometry and focused onto a fiber optic bundle. The output of the fiber optic bundle was coupled to the entrance slit of a Spex Spec-One 500 M spectrometer and detected using a nitrogen-cooled charge coupled device camera.

The red traces in Fig. 4 correspond to the measured THG signals from PFO solution for different values of λ_{OPA}. We found that pure chloroform does not exhibit any THG signals under the same conditions. Note that the measured THG intensity strongly depends on λ_{OPA} in our observation range. The observed sharp drop in the THG intensity near the optical bandgap (see Fig. 1) essentially arises from absorption of the THG light over an extended distance of 12 mm. Although we could not measure THG response for longer wavelengths due to the OPA limitation, our wavelength-dependent THG measurements imply that PFO could be utilized for an active THG generation medium working in the mid-IR range ($\lambda > 2$ μm).

In summary, we have measured the nonlinear refractive index n_2 and three-photon absorption coefficient γ of PFO arising from its third- and fifth-order optical susceptibilities respectively, using Z-scan technique. The $\chi^{(3)}$ response has also been independently confirmed by wavelength-dependent THG. Our results potentially imply that PFO in solid-state forms, including nanowires, can be an attractive organic π-conjugated polymer system for nonlinear optics applications.

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